Biodiesel Production in Fixed-Bed Catalytic Reactors

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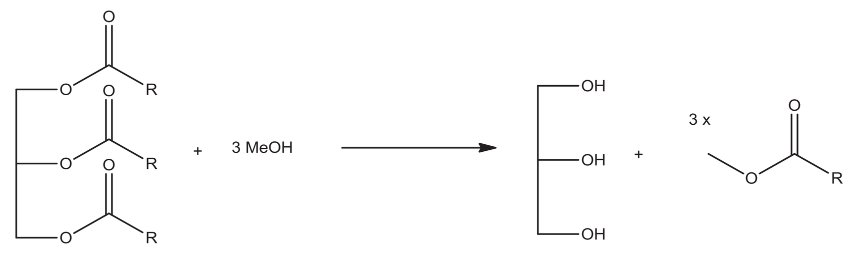
Introduction to biodiesel

Biodiesel is a potentially renewable fuel made by the transesterification of vegetable oils or animal fats with a primary alcohol; in this case methanol is used to make fatty acid methyl esters, or FAME. This can be performed with an acid or base catalyst. As a fuel, biodiesel can be interchanged directly with conventional diesel, and so can be used with the existing infrastructure. Environmental advantages include biodegradability and reduced emissions of volatile organics, carbon monoxide, and particulates[1]. This project aims to develop a continuous reactor with a catalyst supported on a monolith structure.



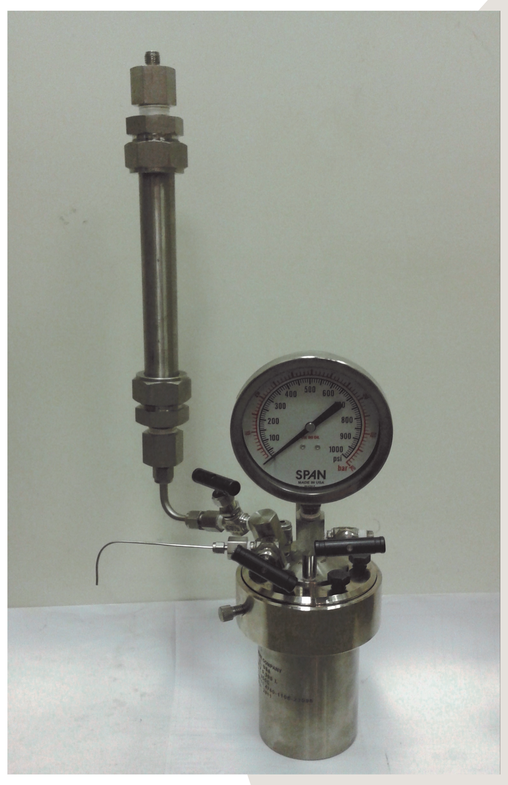
General reaction scheme for the transesterification of triglyceride with methanol. Monoglycerides and diglycerides are produced as intermediate products.

Why heterogeneous catalysis?

Ideally, if a robust and impurity tolerant heterogeneous catalyst can be developed, this will reduce:

- Plant equipment and footprint
- Feedstocks used (catalysts, neutralising agents)
- Waste water and salts
- Production costs

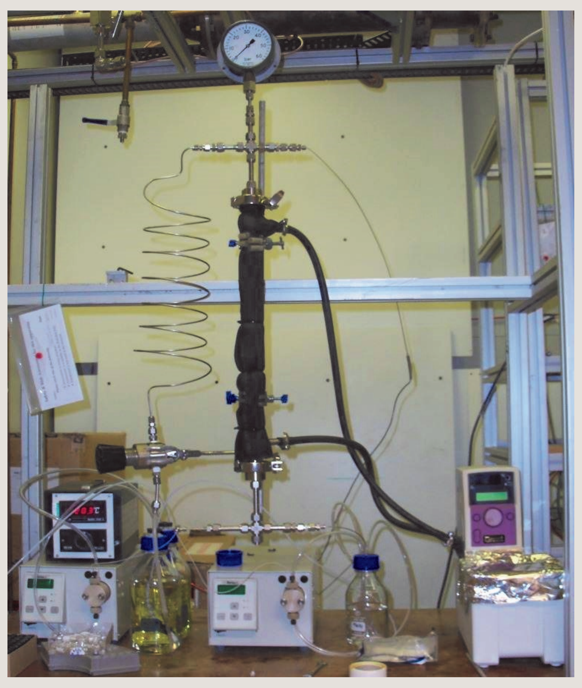
Testing the catalysts



Monolithic catalysts are tested at 120°C in a stainless steel autoclave, with a 6:1 molar ratio of methanol:oil. Samples are taken regularly and analysed by gas chromatography. The results from the most promising candidate are shown in the chart to the right.

Steel reaction vessel for testing potential catalysts. The vertical cylinder can be filled with methanol for pressurised injection to control the starting point of the reaction.

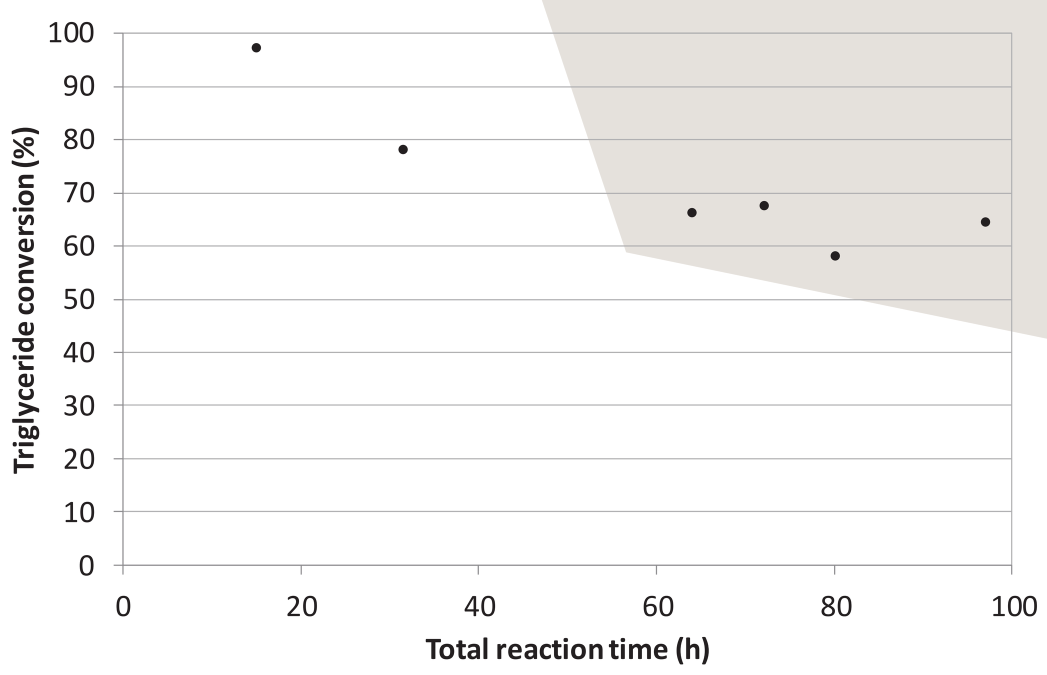
After a successful catalyst has been identified, it is loaded into the continuous reactor. The reactor can reach temperatures of up to 200°C, at pressures up to 20 bar. It has an available bed length of 400 mm.



Continuous reactor for testing monolithic catalysts.

Catalyst lifetime

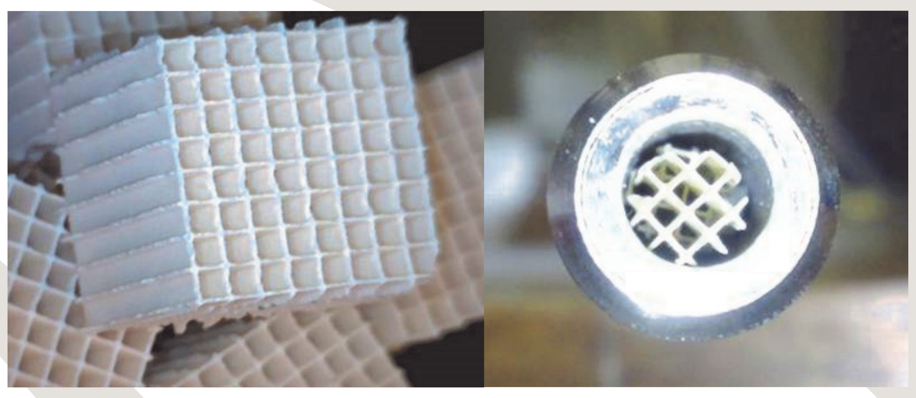
The coated monoliths were tested over the course of three weeks in the continuous reactor. At the end of this, the catalyst still retained activity.



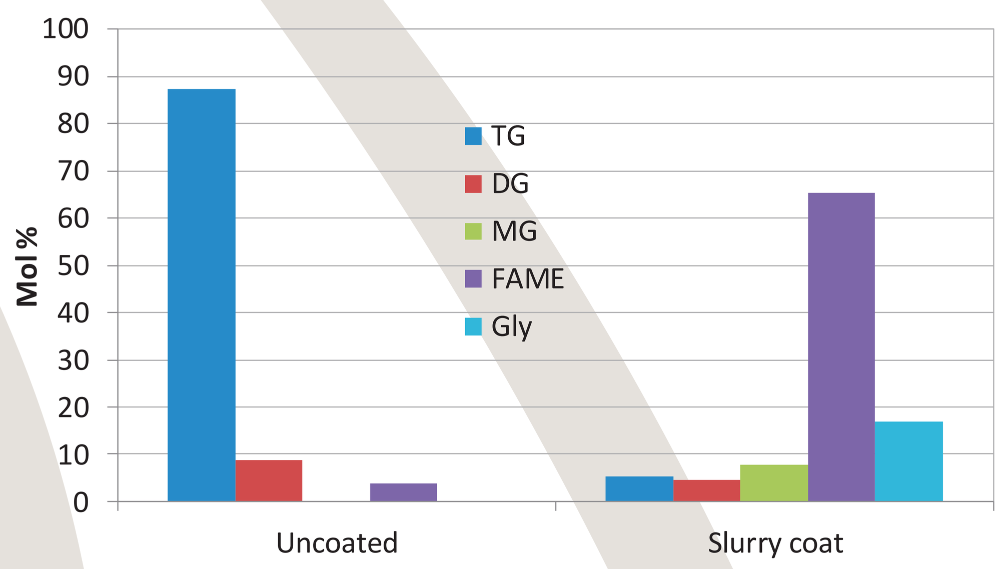
Conversion with time, 200 mm catalyst bed, 195°C, 0.1 ml/min.

Monoliths

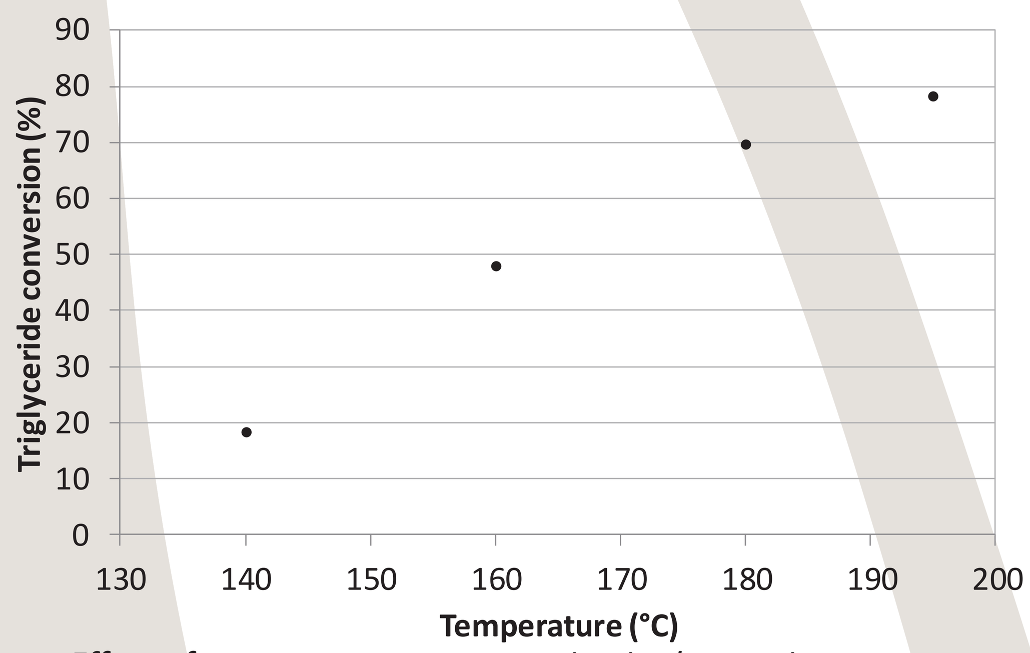
Monoliths are catalyst support structures forming a continuous series of regular channels. These may be coated with additional support material, such as alumina, along with a catalyst. The monoliths used in this project are thin walled cordierite with parallel channels.



Cordierite monoliths, left, and monoliths loaded into the continuous reactor, right.



Products of conversion of vegetable oil to FAME after 24 hours. SrO loading w.r.t. oil is 0.19% (c.f. 1% for typical reaction).



Effect of temperature on conversion in the continuous reactor, 200 mm catalyst bed, 0.1 ml/min.

Slurry coating

The main catalyst of interest is strontium oxide. This has been shown to be a very effective heterogeneous catalyst for transesterification. The monoliths are cut to size and before being coated. A slurry is made by ball-milling strontium hydroxide in water, with some additives to aid adhesion introduced before coating. The monoliths are dipped in the slurry, then dried and calcined at 720°C to form a layer of SrO. SEM images of the catalyst are shown below.

Cutting → **Coating** → **Calcining** → **Catalysis**

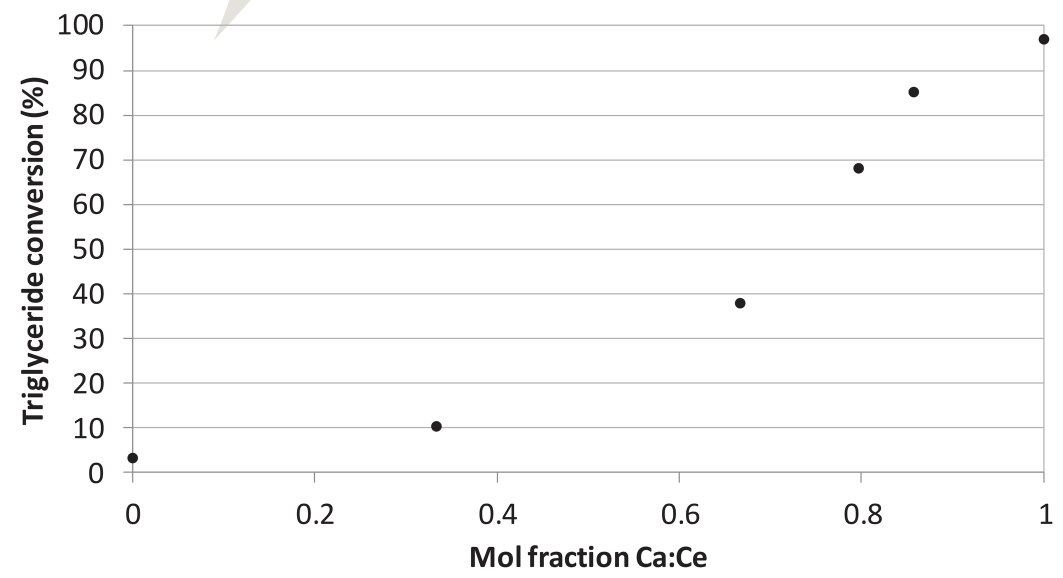
SEM images of the top layer of a slurry coated monolith. In the lower image, mechanical defects can be seen. These lead to structural instability, which will be addressed in future work.

Conclusions and future work

- Strontium oxide is a powerful heterogeneous catalyst
- A coating method has been developed to deposit SrO on a monolithic support
- Catalyst candidates have been tested in a batch reactor
- Reaction in a continuous setting looks promising

Future work:

- Further development of slurry coat, to improve mechanical stability and catalyst lifetime
- Continuous reaction data will be used to test a set of reaction modelling equations that have been developed
- Investigate doped La_2O_3 as a catalyst (see figure on right)



Preliminary batch reaction data for varying proportions of Ca and Ce loaded onto La_2O_3, 65°C, 24h, 1% catalyst loading. It has been reported that doped La_2O_3 is an impurity tolerant and durable catalyst[2].

[1] Bannister, C.D., *et al.*, *Proc. Inst. Mech. Eng.* D J. Automob. Eng., **2010**, *224*, 405-421. [2] Kim, M. *et al.*, *Green Chem.*, **2011**, *13 (2)*, 334-339

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